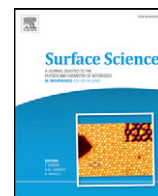




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## The templated growth of a chiral transition metal chalcogenide

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### ABSTRACT

We demonstrate that an intrinsically chiral, high Miller index surface of an achiral metal can be used to template the enantioselective growth of chiral transition metal chalcogenide films. Specifically, Cu(643)<sup>R</sup> can be used as a template for the enantioselective growth of a chiral copper telluride alloy surface. Beyond a critical alloy thickness the chiral influence of the Cu(643)<sup>R</sup> surface diminishes and an achiral surface forms. Our work demonstrates a new method of producing chiral transition metal chalcogenide surfaces, with potential applications in the study of structurally chiral topological insulators.

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### 1. Introduction

Inorganic chiral surfaces play important roles in a number of fields ranging from asymmetric catalysis [1] to speculations on the origins of life [2] and, more recently, the electronic properties of topological insulators [3]. Some naturally occurring minerals, such as quartz, have an intrinsically chiral crystallography that leads to asymmetries in any exposed surface. Chiral interfaces can also be created from achiral crystals by interaction with a chiral ligand via etching [4], electrodeposition [5] or simply via the production of ordered arrays with oblique unit cells [6,7]. Alternatively, a chiral surface can be produced from an achiral metal by exposing low-symmetry, high Miller index surfaces [8] whose kink sites can display enantioselective molecular adsorption [9], desorption and surface chemistry [10–20]. Somewhat surprisingly, there are very few examples of heteroepitaxial growth on such chiral surfaces, despite their technological potential. SrTiO<sub>3</sub>(621) and Pt(321) have both been used as templating substrates for metal thin film growth, with the adsorption of Pt and Cu in the case of SrTiO<sub>3</sub>(621) [20–23] and Au, Ag and Bi in the case of Pt(321) [16]. In each system, there is a general preference for adatoms to occupy the chiral kink sites in the early stages of growth, presumably driven by their higher co-ordination. In contrast, here we consider a more complex epitaxial system that has the potential for surface alloy formation. We demonstrate that chiral, high Miller index surface

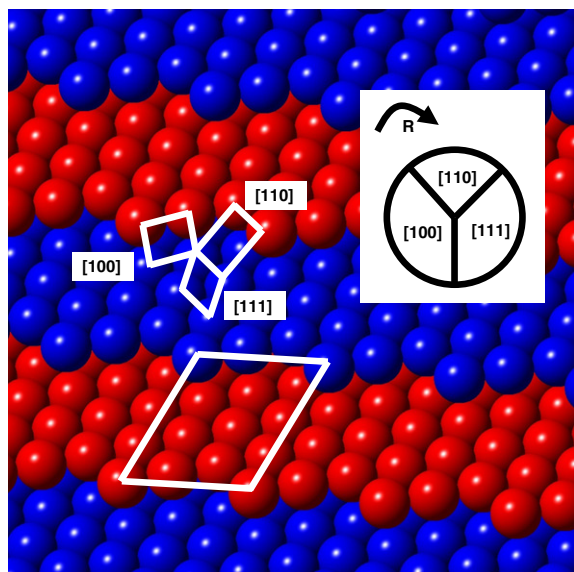
planes of a substrate can act as a template for the growth of nanoscale transition metal chalcogenide films with chiral structures.

The substrate used in this study is Cu(643)<sup>R</sup>, which can be considered to be miscut from a (111) surface, the miscut giving rise to a regular array of (110) kinks and (100) steps, as illustrated in Fig. 1. The chirality of this surface stems from the orientation of kink sites. McFadden et al. [9] first attempted to describe the handedness of chiral surfaces in terms of steps of unequal length; this was later developed by Attard et al. [19], who generalised the Cahn–Ingold–Prelog priority rules [24] with regard to the {hkl} sites surrounding the chiral kink site. In the latter scheme, the handedness of a surface can be assigned depending on the order of rotation from low to higher-index microfacets about a kink site. For example, the clockwise orientation of (100) steps → (110) kinks → (111) terraces illustrated in Fig. 1 is assigned as the R enantiomer. A more rigorous framework for the description of surface chirality has subsequently been developed by Jenkins and Pratt [8] although it is not used here.

Experimental observations demonstrate that in reality the Cu(643)<sup>R</sup> surface has significant deviations from its ideal termination, which is driven towards higher-coordinated, lower surface energy structures by the relatively high mobility of Cu adatoms at room temperature. Density functional theory calculations [25], Monte Carlo simulations [26] and scanning tunnelling microscopy (STM) [27] have shown that the surface undergoes thermal roughening. The result is an inhomogeneous distribution of steps and a larger proportion of (111) terraces, but with kinks of a single handedness that retain the overall chirality imposed by the macroscopic miscut angle [25,26]. This drive towards structures that minimise surface energy can be enhanced by deposition of an overlayer, as has often been observed on achiral, vicinal

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**Fig. 1.** Cartoon of the ideal  $(643)^R$  surface, with downward steps from the top to the bottom of the image. Alternate layers are coloured red and blue to aid visualisation of the surface. The figure shows the unit cells of the micro facets: the step site is [100], the kink site is [110] and the terrace is [111]. The handedness of the surface is defined as indicated by the schematic in the top right, which here indicates a clockwise orientation of priority, from [100] steps to [110] kinks then [111] terraces, and is assigned as the R-enantiomer [18]. The parallelogram at the bottom of the image indicates the  $(643)$  unit cell. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(i.e. stepped) surfaces. Most notably, deposition of metallic Ag on Cu(223) induces a periodic faceting of the underlying Cu surface into a “hill and valley” structure [28–32], whilst adsorption of oxygen and sulfur are both known to drive substantial mass-transfer and faceting of Cu surfaces [33–38]. These systems can be expected to have similarities with the deposition of Te, a metalloid chalcogen, as will be described here. However, a significant difference between the present study and previous thin film growth on chiral substrates is that we observe alloying and the formation of the compound copper telluride as a nanoscale film. The present study therefore provides a unique method for the production of chirally-structured transition metal chalcogenide films, which are potentially useful models for the study of chirality in the electronic properties of topological insulators.

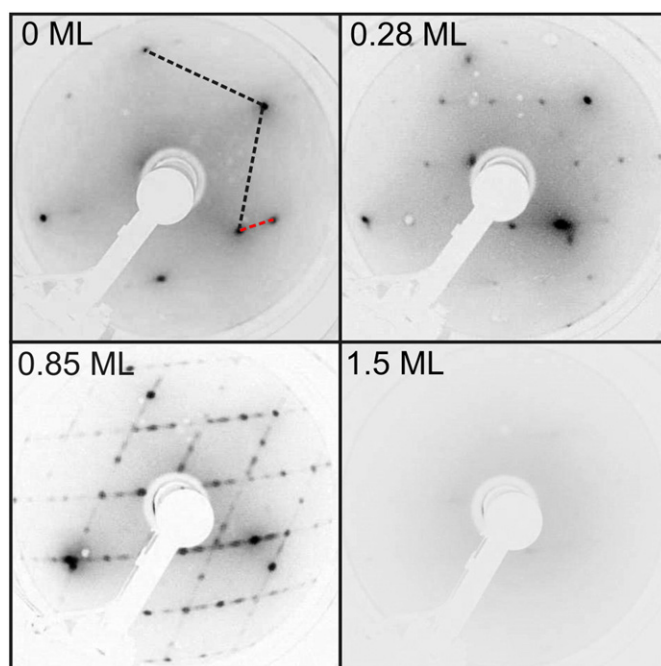
## 2. Experimental

Measurements were performed in two separate UHV systems, both with an operating pressure of  $2 \times 10^{-10}$  mbar. The first chamber was equipped with a discharge lamp (VG Scienta Ltd.) which provides He(I) radiation for ultraviolet photoemission spectroscopy (UPS) and an Al  $K_{\alpha}$  X-ray source (VG Scienta Ltd.) for x-ray photoemission spectroscopy (XPS). Spectra were collected using a concentric hemispherical analyser (CLAM 2, VG Scienta Ltd.) aligned along the macroscopic normal of the  $\text{Cu}(643)^R$  surface. The second chamber was used to collect STM data. STM images were obtained using an Omicron STM-1 with MATRIX software, using an etched W tip with a positive bias in constant height mode. The  $\text{Cu}(643)^R$  sample was cleaned *in-situ* by repeated cycles of  $\text{Ar}^+$  bombardment (1 kV, 8  $\mu\text{A}$ ) and annealing to 830 K. Sample cleanliness and crystallinity were verified by XPS and LEED. Te was deposited from a homemade Knudsen effusion cell. For sub monolayer (ML) films, the typical cell temperature was 570 K. The deposition rate for sub monolayer films was calculated from Cu  $2p^{3/2}$  and Te  $3d^{5/2}$  XPS intensities to be  $\sim 0.2$  ML  $\text{min}^{-1}$ . For film thicknesses greater than 10 ML, a cell temperature around 610 K was used, giving a deposition rate of  $\sim 5$  ML  $\text{min}^{-1}$ . Te coverages quoted

here have an approximate error of  $\pm 0.05$  ML and are given with respect to the atomic density of the  $\text{Cu}(111)$  surface.

## 3. Results

The LEED pattern obtained from an atomically clean  $\text{Cu}(643)^R$  surface is shown in the first panel of Fig. 2 and is assigned as  $\text{Cu}(643)^R$  by comparing it to a  $\text{Pt}(643)^R$  pattern reported previously [8]. The pattern can be considered as an off-axis 6-fold pattern of split spots, with the off-axis 6-fold pattern arising from the (111) terraces of Fig. 1 and the spot splitting arising from the longer-range periodicity of the stepped surface [8,19,39]. This spot splitting breaks the symmetry of the LEED pattern and the angle of the doublet with respect to the 6-fold pattern can be used to assign surface chirality [8]. Images of LEED patterns collected after room temperature deposition of up to 1.5 ML are displayed in subsequent panels of Fig. 2. All of these patterns were collected after the surface was annealed at 773 K for 10 min, then allowed to cool slowly back to 110 K, a procedure adopted because patterns collected immediately after deposition at 300 K were diffuse, implying a significant amount of disorder and/or surface mobility. Notably, the annealing process does not change the chemical identity of the surface for low coverages, since there was no induced change in peak shape or intensity in the XPS spectra. Thus, it is likely that local ordering occurs immediately upon deposition, but at a length scale too small to be observed with LEED, and perhaps with a number of isolated defects that attenuate coherent electron scattering in LEED. Surface homogeneity then improves with annealing, suggesting that the substantial mass transfer associated with the faceting reconstructions described below is kinetically limited at room temperature. An overview of Cu  $2p^{3/2}$  and Te  $3d^{5/2}$  XPS spectra, corresponding roughly to the coverages of Fig. 2 and collected at a sample temperature of 300 K, is shown in Fig. 3. Each Te  $3d^{5/2}$  and Cu  $2p^{3/2}$  spectrum was fitted to the sum of Gaussian and Doniach Sunjic (DS) functions [40] and the fitted binding energies were in agreement



**Fig. 2.** LEED patterns obtained for increasingly thicker Te films on  $\text{Cu}(643)^R$ , recorded at a sample temperature of 110 K. The top left panel shows the clean  $\text{Cu}(643)^R$  surface with the dashed black line indicating part of the  $(643)^R$  surface unit cell. The dashed red line shows that the  $(0,1)$  spot has been split by a length inversely proportional to the step separation. All spots in the clean  $\text{Cu}(643)^R$  pattern are split, however, they are difficult to see at a single beam energy. The beam energy in all images is 138 eV. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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